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NITROSO INTERMEDIATES IN ELECTROLYTIC REDUCTION OF NITROALKANES

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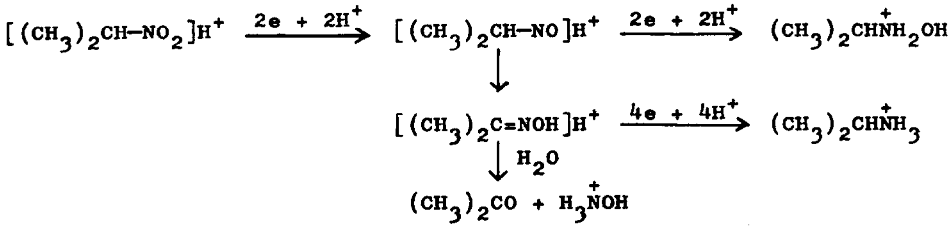
The electrolytic reduction of aliphatic nitro compounds is generally postulated to proceed through the nitroso stage (1,2,3). As this intermediate is reduced at a less negative potential than the parent nitro compound, it does not accumulate during the electrolysis, and the evidence for its formation is indirect. Only in a single instance, the reduction of chloropicrin in methanolic sulphuric acid (4), the isolation of a nitroso compound has been reported. Below is presented direct and indirect evidence for the presence of a nitroso derivative during the electrolytic reduction of aliphatic nitro compounds.

In macro-scale electrolytic reductions of primary and secondary nitroalkanes (5) no nitroso derivative has been detected polarographically during the reaction; however, in a similar reduction of t-nitrobutane (40.0 ml = 0.368 mole) at 20-25° at potentials less negative than −1.0 V vs SCE in 3 N 50 % alcoholic hydrochloric acid a polarographic wave ($E_{\frac{1}{2}}$ approx. −0.1 V vs SCE) could be detected directly in the catholyte; t-nitrosobutane (dimer (6)) gives a polarographic wave at the same potential under these conditions. Furthermore, the catholyte turned blueish-green during the reduction, showing a broad absorption maximum about 280 mμ; t-nitrosobutane (dimer) has λ_{max} = 288 mμ in N hydrochloric acid. The colour of the catholyte disappeared during some minutes on interruption of the current due to acid hydrolysis of the tertiary nitrosoalkane (7); this hydrolysis made a quantitative determination of the t-nitrosobutane dubious.

The reduction of *t*-nitrobutane consumed approximately 4 electrons per molecule (40 Ah); analysis of the catholyte (5) gave 90-95 % of *t*-butylhydroxylamine, 1-3 % of alkylamine, and below 0.5 % of starting material. No attempts were made to detect the small amount of *t*-butanol resulting from acid hydrolysis of the intermediate *t*-nitrosobutane (7).

The *t*-butylhydroxylamine was isolated as the white, non-hygroscopic hydrochloride in 80-90 % yield by evaporating the catholyte to dryness *in vacuo* at temperatures below 50°, dissolving the residue in hot abs. ethanol, and precipitating the hydrochloride with ether, m.p. 182.5-183° (uncorr., abs. ethanol-ether). (Found: C 38.55; H 9.55; N 10.90. Calc. for $C_4H_{12}ClNO$: C 38.30; H 9.65; N 11.16). The ready availability of *t*-nitrobutane (8), the high yield, and the easy isolation of the product make the electrolytic preparation of *t*-butylhydroxylamine an attractive alternative to the synthesis through acid hydrolysis of *t*-butyloxazirane (9), and the hydrochloride is much easier to handle than the rather unstable free *t*-butylhydroxylamine (9).

Although no direct proof of a nitroso intermediate has been found in the electrolytic reduction of primary and secondary nitroalkanes, the isolation of carbonyl compounds from such reactions is indirect evidence. Thus, from controlled potential reduction of 2-nitropropane, acetone was isolated as the 2,4-dinitrophenylhydrazone, m.p. (uncorr.) 125-127° (128° (10)) in 8 % yield. The formation of acetone is readily explained from the general reduction scheme proposed by Masui *et al*. (3)



$$\begin{tikzcd}
{[(CH_3)_2CH{-}NO_2]H^+} \arrow[r, "2e\,+\,2H^+"] & {[(CH_3)_2CH{-}NO]H^+} \arrow[r, "2e\,+\,2H^+"] \arrow[d] & (CH_3)_2CH\overset{+}{N}H_2OH \\
 & {[(CH_3)_2C{=}NOH]H^+} \arrow[r, "4e\,+\,4H^+"] \arrow[d, "H_2O"] & (CH_3)_2CH\overset{+}{N}H_3 \\
 & (CH_3)_2CO + H_3\overset{+}{N}OH &
\end{tikzcd}$$

A typical electrolytic reduction of 2-nitropropane (5) would thus yield 86 % of isopropylhydroxylamine, 5 % of isopropylamine, 8 % of acetone, and below 1 % of starting material. Varying amounts of carbonyl compounds have been isolated (as the 2,4-dinitrophenylhydrazones) from the electrolytic reduction of other nitroalkanes.

The occurrence of alkylamines as products from electrolytic reduction of nitroalkanes (e.g. 11) also presents indirect evidence for a nitroso intermediate as the amine cannot be formed from the hydroxylamine by reduction in acid medium. Thus, electrolysis of 5 g of N-methylhydroxylamine hydrochloride at −1.15 V vs SCE in hydrochloric acid at 20-30° for 16 h (with hydrogen evolution) gave no detectable amount of amine (5), and polarographic investigation of N-isopropylhydroxylamine oxalate showed the presence of a cathodic wave at $E_{\frac{1}{2}}$ = −1.55 - −1.75 V vs SCE only in the pH-interval 5-9 in accordance with Petru's experiments (12) on N-methylhydroxylamine. However, acetoxime is polarographically reducible ($E_{\frac{1}{2}}$ = −1.05 V vs SCE, pH = 0.2), and isopropylamine has been isolated in 66 % yield from reduction below 20° at a lead cathode in 50 % sulphuric acid (13), so it seems quite reasonable to accept that amine formation proceeds only through a nitroso intermediate, either by reduction of the oxime or by reduction of the imidonium ion intermediate suggested by Masui et al. (2,3). This view is also in accordance with the fact that the amine is the main product from primary and secondary nitroalkanes at higher temperatures (11) where the rearrangement to the oxime is faster. No significant changes of the catholyte composition were found in electrolytic reduction of t-nitrobutane at room temperature and at 60-70°. Thus, the most important factor to determine whether nitroalkanes are reduced to hydroxylamines or amines at a mercury electrode at controlled potential seems to be the temperature and not, as suggested (14), the overvoltage of the cathode material.

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